

PATENT SPECIFICATION

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(54) HYDROGEN

5 (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for producing hydrogen by reacting carbon monoxide with steam over a catalyst active at below 300°C, and especially to such a process forming part of a combination of steps including, upstream of the carbon monoxide/steam reaction stage, a high temperature reaction of a carbonaceous feedstock with steam.

15 The production of hydrogen by the catalytic shift reaction of carbon monoxide with steam has been used, most commonly containing iron oxide, have been active only at temperatures above about 350°C, at which the concentration of carbon monoxide cannot be economically decreased below about 3% by volume. More recently the shift reaction has been carried out at lower temperatures such as 20 170—300°C and has enabled the carbon monoxide content to be economically decreased to 0.5% by volume or less, such that it can be finally removed by methanation without incurring excessive hydrogen loss. Catalysts for the low temperature shift reaction have been known for many years, but their industrial use has become gradually more practicable 25 only as the problems of manufacturing them and using them have been overcome by such measures as choice of promoter oxide and avoidance of sulphur poisoning, respectively. Despite the precautions which are now taken, low temperature shift catalysts still have a 30 reputation for losing activity in use. Since it is still quite common for manufacturers of such catalysts to have to replace batches because performance guarantees were not fulfilled, it is evident that uncontrolled factors must still be at work.

35 We have found that poisoning by halogen, especially chlorine, is one of such hitherto uncontrolled factors and that the shift catalyst

can be protected from it by means which forms the basis of this invention.

40 According to the invention a process for producing hydrogen by reacting carbon monoxide with steam at under 300°C over a copper-containing low temperature shift catalyst in discrete pieces is characterised in that the catalyst is preceded by a bed of discrete pieces of a solid guard material that is more basic than zinc oxide or in that such guard material and such catalyst are in admixture.

45 The solid material more basic than zinc oxide conveniently can contain a basic compound of any element of Group IA or Group IIA of the Periodic Table (other than beryllium) or of for example a rare earth such as yttrium or lanthanum having a compound which is basic enough. Preferably the compound should be an oxide, hydroxide or a carbonate, so as not to introduce interfering by-products into the reaction system. Since the quantity of halogen present and the quantity needed to poison the catalyst are extremely small it is often sufficient to use a compound or adsorption complex of an alkali metal or alkaline earth metal with an inorganic polymer such as a clay, or even an ion exchange resin. Which basic compound is used depends on how the solid basic material is brought into contact with the gas containing carbon monoxide and steam, as will be described in detail hereinafter. The basic material is very conveniently used as a composition in which it is supported on a catalyst carrier material. For example an alkali metal compound supported on discrete pieces of alumina can be used; the alumina preferably has a moderate specific surface (that is, 5—200 m²/g) and the alkali concentration calculated on the total of alkali metal compound and carrier is preferably in the range 0.5 to 5% by weight calculated as equivalent sodium oxide Na₂O.

50 The solid material more basic than zinc oxide can be disposed in a guard bed upstream of the low temperature shift catalyst. It has previously been proposed to provide a space for a desulphurisation guard bed, usually con-

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sisting of zinc oxide, just upstream of the low temperature shift catalyst: it is convenient to use this space for the solid guard material if it is not in fact used for desulphurisation, or 5 to replace the desulphurisation material wholly or partly by the solid guard material. The solid guard material can if desired lie immediately in contact with the bed of low temperature shift catalyst. If the discrete pieces of guard 10 material are in admixture with the discrete pieces of low temperature shift catalyst, the discrete pieces of guard material may be of a size such that they can be readily separated from those of the shift catalyst by for example 15 sieving.

In an important form of the invention a catalyst bed is used the inlet portion of which is formed by a guard material containing copper and zinc oxide (and preferably also 20 an oxide of a metal from Groups II to VII of the Periodic Table as set forth in "Abridgments of Specifications") and a quantity of a basic compound of an alkali metal equivalent to a sodium oxide (Na_2O) content between 25 0.25 and 1%, especially 0.3 and 0.6% by weight calculated on the guard material containing copper oxide from which the guard material is formed by reduction. The remainder of the bed contains a low temperature 30 shift catalyst but contains less than 0.25% by weight of the basic alkali metal compound, calculated in the same way. This form of the invention departs from the normal practice in low temperature shift technology, in which alkali contents greater than 35 corresponding to 0.25% by weight of sodium oxide are considered undesirable owing to the shortened catalyst life which has been attributed to the alkali. The two parts of the bed may 40 be in contact or may be mechanically separate.

The basic alkali metal compound of the copper containing guard material of the inlet portion of the catalyst bed can have been introduced for example as the carbonate, bis 45 carbonate, hydroxide or as a compound that decomposes thereto under shift reaction conditions. It can have been introduced by deliberate addition to the corresponding low-alkali material or, if the material is of the 50 type made by way of a precipitation involving an alkali metal compound, such as a carbonate, can have been allowed to remain in the precipitate by adopting a less rigorous washing procedure.

55 As an alternative to the alkali metal compound in such a copper containing guard material other solid compounds more basic than zinc oxide in halogen-absorbing quantities may be present in particular basic compounds 60 pounds of calcium, strontium or barium; the concentration of such other basic compounds can be for example, 0.2 to 0.5% by weight calculated as equivalent Na_2O on the composition containing copper oxide from which 65 this guard material is formed by reduction.

If desired discrete pieces of, the guard material and of the catalyst may be in admixture, but this is less convenient.

When the shift catalyst contains copper and zinc oxide, its proportions need not be changed from those which have been recently proposed or used, for example containing up to about 70% of copper by metal atoms of the total copper and zinc, especially 10—50% copper. Usually zinc is in excess of copper, especially up to a ratio of about 6:1 by atoms, and commonly about 1.5 to 2.5. Suitable shift catalysts and low temperature processes using them are described in UK Patent 1,131,631.

The invention is especially applicable to low temperature shift processes when applied to the gas produced by reacting a carbonaceous feedstock with steam at high temperature, passing the crude gas through a waste-heat boiler and then subjecting the gas to further processing steps to convert it into synthesis gas or hydrogen for hydrogenations. Since an over-all process of this type is made more viable and economic by using the process of the invention, the over-all process also is an embodiment of the invention. In particular, thus, the invention provides a process for producing hydrogen in which a hydrocarbon feedstock is endothermically reacted with steam at a temperature in the range 600—10000°C, to give a gas containing carbon monoxide and hydrogen, the gas is passed through one or more waste-heat boilers in which it gives up sensible heat, the gas is cooled to shift inlet boilers in which it gives up sensible heat, the gas is cooled to shift inlet temperature, the cooled gas is subjected to shift conversion over a copper-containing catalyst in discrete pieces at a temperature of under 300°C, and the shift conversion over a copper-containing catalyst in discrete pieces at a temperature of under 300°C, and the shift outlet gas is treated to remove carbon dioxide and catalytically methanated to convert any residual carbon oxides to methane, characterised in that the low temperature shift catalyst is protected from poisoning by traces of halogen in the gas by contacting the gas with discrete pieces of a solid material more basic than zinc oxide.

Such a process can be based on a gaseous feedstock such as methane or butane or refinery gas or a liquid feedstock such as naphtha. The endothermic reaction of such feedstocks with steam can be in a single stage, such as by tubular steam reforming, non-catalytic partial oxidation or catalytic partial oxidation; preferably it consists of an initial tubular steam reforming stage, followed where appropriate by secondary reforming in the presence of added air, whereby the nitrogen required for ammonia synthesis gas is introduced. The waste heat recovery section may produce steam at substantially above process pressure, for example at 1000—2000 psig when the

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process is operated at 150-600 psig. The gas can be cooled to shift inlet temperature by the waste-heat boilers alone or part of the cooling may be effected by means of quench steam or water. A high temperature (e.g. 350-500°C) shift stage over for example an iron-chromia catalyst may be used before the low temperature shift stage in order to decrease the carbon monoxide content of the gas to a level — about 1-4% — at which the low-temperature shift catalyst may be used without an excessive temperature rise. Often the gas is cooled between the high temperature and low temperature shift stages by means of a waste heat boiler or boiler feed water heater.

EXAMPLE 1.

A guard material was made by impregnating 600 g. of discrete pieces, viz. cylindrical pellets, of gamma alumina (3/16 inch by 3/16 inch) at room temperature with 240 ml. of a solution containing 10.6 g. of sodium hydroxide. The pellets were dried, then calcined at 700°C. Their sodium oxide content was 1.2% w/w and their specific surface 60 square metres per gram.

The pellets were tested for chlorine-absorption by charging them to a laboratory tubular

reactor as 5 successive beds separated by glass wool, then passing over them a shift inlet gas having the dry gas percentage composition by volume,

H ₂	60	30
N ₂	20	
CO ₂	16	35
CO	4	

and a steam ratio 0.5, at a space velocity of 12000 hour⁻¹, the temperature being 230°C and the pressure atmospheric. The steam contained 10 ppm of natural chloride and 0.25 ppm of Cl-36, both forms being introduced as hydrochloric acid into the water feed to the capillary boiler from which the steam supply was derived. After 7 day's running, during which the chlorine content of the water condensed from the outlet gases was just detectable (one millionth of a part per million), the gas flow was stopped and the 5 absorption beds analysed: for the analysis the beds were washed by boiling repeatedly with potassium hydroxide solution, whereafter the dissolved chlorine contents were estimated by liquid scintillation counting. From these chlorine contents the bed chlorine contents were calculated to be as follows:

Bed	1 (inlet end)	2	3	4	5 (outlet end)
Cl%	0.37	0.33	0.0033	0.0012	0.0007

It is evident that chloride is tenaciously absorbed by the alkali-treated alumina and would be prevented from reaching any catalyst downstream of it.

EXAMPLE 2.

Two beds of commercially available copper/zinc oxide/alumina low temperature shift catalyst were set up in parallel, one being preceded by a guard bed of sodium hydroxide/alumina as described in Example 1, the other by a bed of alumina to which alkali had not been added.

Then the same gas mixture as was used in Example 1 without, however, any deliberate chlorine addition, was passed over the two beds at atmospheric pressure, a temperature of 230°C and a space velocity of 15000 hour⁻¹. The outlet gas was analysed for carbon monoxide and the results used to calculate a first-order reaction velocity constant (reciprocal seconds) representing the activity of the catalyst. The Table shows the variation of activity during a run of lasting 360 hours.

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TABLE 1

Time (hours)		3	20	69	95	196	370
Activity Sec ⁻¹	without guard bed	7.8	6.5	5.4	4.7	4.1	3.8
	with guard bed	7.5	7.1	6.1	4.9	5.6	6.2

It is evident that the guarded catalyst has maintained its activity to a substantially better extent than the unguarded catalyst.

EXAMPLE 3.
In an ammonia plant in Canada which in-

cluded a natural gas/stream reforming stage, a high-temperature shift stage, a cooler, a low temperature shift stage, a CO₂ — removal stage and a methanation stage, the charge of substantially alkali-free low temperature shift catalyst, which had lost activity down to 25%,

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of its initial level over a period of less than one year, was replaced by a two-part charge of a catalyst made by reducing *in situ* a composition comprising copper oxide (33%), zinc oxide (53%) and alumina (14%) all these percentages being by weight. The inlet portion of the charge (14% of the total volume) constituting the guard material contained 0.5% of alkali by weight calculated as Na_2O on the total of copper oxide, zinc oxide and alumina. The remainder contained only 0.09% of alkali, calculated in the same way.

The low temperature shift stage was operated at an inlet temperature of 216°C, pressure 350 psig, steam-gas volume ratio of 0.55 and dry gas volume space velocity of 3000 hour^{-1} . The inlet carbon monoxide concentration was 2.5% on a dry gas basis and the outlet carbon monoxide concentration was 0.16%, both by volume.

After 24 months' service the performance of the low temperature shift stage had undergone no measurable change.

EXAMPLE 4.

25 Effectiveness of polyvalent basic compounds as guard materials

Guard materials were made by impregnat-

ing squat cylindrical pellets (3.6 by 5.4 mm) of gamma alumina with the nitrates of respectively calcium, barium, manganese, yttrium and lanthanum, then drying and calcining at 700°C.

The pellets were tested in a laboratory tubular reactor containing 5 successive 25 ml beds each separated by glass wool, the first 4 beds consisting of guard material and the last being a 25 ml bed of commercially available copper/zinc oxide/alumina low temperature shift catalyst. Shift inlet gas consisting of steam (33.3%), hydrogen (53.4%), carbon dioxide (10%) and carbon monoxide (3.3%), all by volume, was passed at 230°C at atmospheric pressure through the assembly of beds. The dry gas volume space velocity in each bed was 12000 h^{-1} . At the inlet the total chloride concentration (natural doped with Cl-36) was 1.33 to 2.24 ppm v/v. The tests were run for 5-7 days, during which the catalyst activity was monitored and after which the guard and catalyst bed were analysed as in Example 1. In the outlet gas chloride was just detectable (10^{-3} ppm v/v). Table 2 shows the chloride contents and catalyst activities.

TABLE 2

Guard material (% by weight)	CaO 2.9%	BaO 4.6%	MnO 7.8%	Y_2O_3 1.2%	La_2O_3 1.1%
Cl ⁻ , ppm v/v in let gas	1.79	1.79	2.24	1.42	0.94
w/w Bed 1	0.279	0.326	0.199	0.177	0.115
2	0.195	0.187	1.460	0.130	0.079
3	0.107	0.072	0.095	0.085	0.045
4	0.052	0.017	0.053	p.050	0.021
Catalyst	0.0265	under 0.002	0.045	0.064	0.014
Activity, sec ⁻¹ days 0	7.8	8.5	8.0	—	—
1	—	—	7.8	8.8	9.2
2	—	—	8.0	8.4	8.7
3	7.7	8.0	8.0	—	—
4	7.7	8.0	8.1	—	—
5	7.7	8.0	8.0	7.4	—
6	7.5	8.0	—	6.6	8.2
7	6.6	8.0	—	6.2	8.5

It is evident that each guard material has effectively absorbed chloride and kept the loss in catalyst activity at a low level.

A 25 ml bed of the same low temperature shift catalyst was tested under the same conditions without a guard material. The

chloride content of the inlet gas averaged over the 8 days of the test was 0.83 ppm v/v (1.25 ppm v/v on a dry basis). Table 3 shows the loss of activity of this unguarded catalyst when poisoned under these conditions.

TABLE 3

Time on line days	Activity sec. ⁻¹
0	8.8
1	8.5
2	8.2
3	7.9
4	6.8
5	5.6
6	5.0
7	4.6
8	4.0

WHAT WE CLAIM IS:—

1. A process for producing hydrogen by reacting carbon monoxide with steam at under 300°C over a copper-containing low temperature shift catalyst in discrete pieces characterised in that the catalyst is preceded by a bed of discrete pieces of a solid guard material that is more basic than zinc oxide or in that such guard material and such catalyst are in admixture.

5 2. A process according to claim 1 in which the solid guard material contains a basic oxide, hydroxide or carbonate.

3. A process according to claim 1 or claim 15 2 in which the solid guard material comprises a basic compound supported on a catalyst carrier material.

4. A process according to claim 3 in which the catalyst carrier material is alumina.

20 5. A process according to claim 4 in which the basic compound concentration calculated on the total of basic compound and carrier material is in the range 0.5 to 5% by weight calculated as equivalent sodium oxide.

25 6. A process according to claim 1 or claim 2 in which a guard material containing copper and a basic compound of an alkali metal in a concentration equivalent to a sodium oxide content between 0.3 and 0.6% by weight forms the inlet portion of a shift catalyst bed and the remainder of the bed contains the low

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temperature shift catalyst but contains less than 0.25% by weight of basic compound calculated as aforesaid.

7. A process for producing hydrogen in which a hydrocarbon feedstock is endothermically reacted with steam at a temperature in the range 600—1000°C, to give a gas containing carbon monoxide and hydrogen, the gas is passed through one or more waste-heat boilers in which it gives up sensible heat, the gas is cooled to shift inlet temperature, the cooled gas is subjected to shift conversion over a copper-containing catalyst in discrete pieces at temperature of under 300°C, and the shift outlet gas is treated to remove carbon dioxide and catalytically methanated to convert any residual carbon oxides to methane, characterised in that the copper containing catalyst is protected from poisoning by traces of halogen in the gas by contacting the gas with discrete pieces of a solid material more basic than zinc oxide.

8. A process according to claim 1 substantially as described and as set forth in any one of the foregoing Examples.

9. Hydrogen or synthesis gas whenever produced by a process according to any one of the preceding claims.

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